CALORIMETRIC METHOD FOR EXPERIMENTAL DETERMINATION OF EMISSIVITY OF SOLIDS

S. G. Agababov and V. S. Agababov

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The effect of experimental conditions on the accuracy of a determination of the emissivity of solids by the calorimetric method is discussed.

The calorimetric method for determination of the emissivity of solids is based on a solution of the problem of radiative heat transfer between solids. One of the ways of realizing this method involves consideration of radiative heat transfer between solids such that one, the convex one, is within a cavity of the other, the concave one (for example, a sphere within a sphere or a cylinder within a cylinder). In the case of closed systems, or of neglect of end effects, and for diffuse emission and reflection, the amount of heat which one body supplies to the other is [1]

$$Q = \frac{\sigma_0 [(\varepsilon_1/A_1) T_1^4 - (\varepsilon_2/A_2) T_2^4] F_1}{1/A_1 + (F_1/F_2)(1/A_2 - 1)}, \tag{1}$$

where $\sigma_0 = 5.672 \cdot 10^{-8}$ $W \cdot m^{-2} \cdot {}^\circ K^{-4}$ is the Stefan–Boltzmann constant; F, T, ε, and A are, respectively, the surface area, m^2, the absolute temperature, °K, the integral emissivity, and the integral absorptivity of the internal body 1 and the shell 2. It is assumed that $T_1 > T_2$.

The conditions for obtaining this expression (and also for performance of an experiment) also include the following: stationarity of the heat-transfer process, isothermality of surfaces 1 and 2, transparency of the medium between bodies 1 and 2 to the radiation, and the absence (or inclusion) of a convective component of heat transfer.

The present difficulty in the use of Eq. (1) for experimental determination of the emissivity of a body is explained by the absence of data on the integral absorptivity of solids. The complexity of its study is connected with its dependence on the spectrum of incident radiation. Therefore, one usually assumes equality of emissivity and absorptivity. The latter occurs in the case of "gray" bodies.

In realizing apparatus with a small area ratio F_1/F_2, one neglects the latter by assuming it to be zero. As a result of these assumptions, Eq. (1) is transformed to

$$Q = \varepsilon_1 \sigma_0 (T_1^4 - T_2^4) F_1. \tag{2}$$

In such a situation, this expression is the starting point for the experimental determination of the emissivity value ε_1^{ex}. However, the spectrum from actual solids (especially pure metals) differs from a "gray" spectrum and therefore the experimental value ε_1^{ex} for the emissivity based on Eq. (2) can differ significantly from the real value.

The present paper is devoted to a determination of the influence of various parameters — geometric, physical, and operational, i.e., experimental conditions — on the accuracy of a determination of emissivity.

The error can be evaluated by determination of the ratio between the experimental and actual values of the emissivity. For this purpose, an expression for the experimental value ε_1^{ex} is obtained from Eq. (2) and for the actual value ε_1 from Eq. (1) and the ratio between the first and second taken for otherwise identical conditions (equal values of the thermal flux Q and of other parameters). We then have

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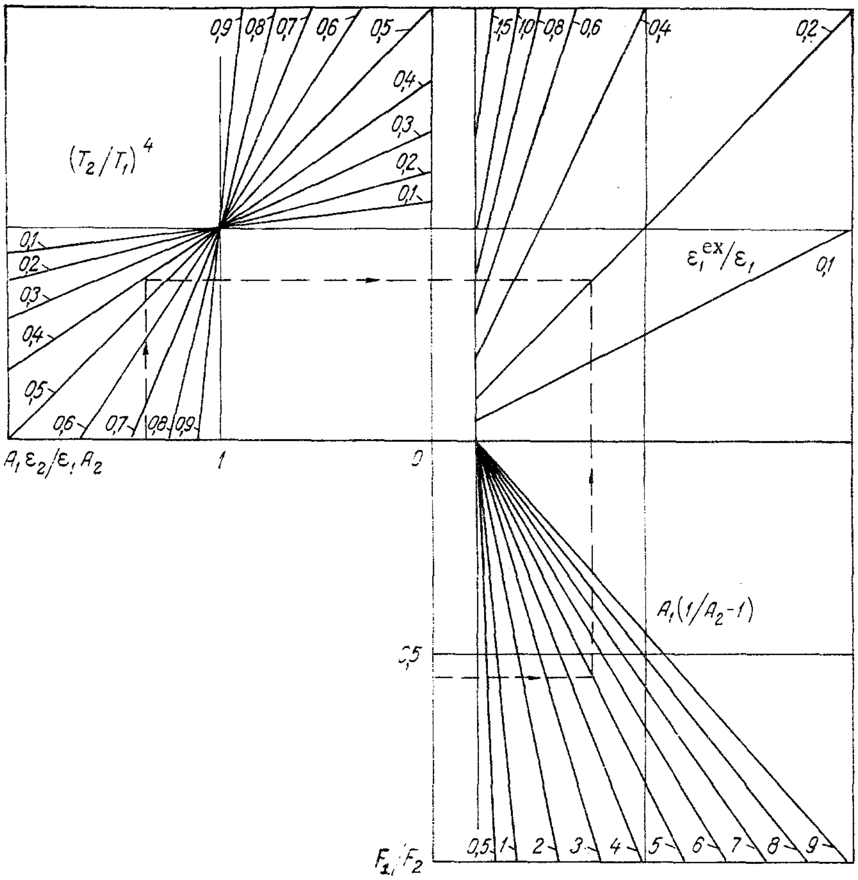

Fig. 1. Dependence of the ratio between experimental and actual values of emissivity on geometric, physical, and operational parameters [calculated from Eq. (3)].

$$\frac{\varepsilon_1^{ex}}{\varepsilon_1} = \left[1 - \frac{A_1}{\varepsilon_1}\cdot\frac{\varepsilon_2}{A_2}\left(\frac{T_2}{T_1}\right)^4\right]\left\{\left[1-\left(\frac{T_2}{T_1}\right)^4\right]\left[1+\frac{A_1}{A_2}(1-A_2)\frac{F_1}{F_2}\right]\right\}^{-1}. \qquad (3)$$

The deviation of the experimental values ε_1^{ex} from the true values ε_1 can be calculated from Eq. (3) as a function of the quantities

$$\frac{T_2}{T_1},\ \frac{F_1}{F_2},\ \frac{A_1}{\varepsilon_1}\cdot\frac{\varepsilon_2}{A_2},\ A_1(1/A_2-1).$$

All the specified parameters, of which the ratio $\varepsilon_1^{ex}/\varepsilon_1$ is a function, must be greater than zero. Calculated results for the specified functional relationships are presented in Fig. 1 in the form of a nomogram [2].

The diagram makes it clear that marked deviation of experimental values ε_1^{ex} from actual values ε_1 are possible under certain experimental conditions.

Thus for $A_1\varepsilon_2/\varepsilon_1A_2 > 1$ (in this case, $\varepsilon_1^{ex}/\varepsilon_1 < 1$ always), the deviation of the experimental value ε_1^{ex} from the actual value ε_1 will be greater the greater the ratios T_2/T_1 and F_1/F_2 and the greater the value of the quantities $A_1(1/A_2 - 1)$ and $A_1\varepsilon_2/\varepsilon_1A_2$. On the other hand, the smaller these quantities are and the closer $A_1\varepsilon_2/\varepsilon_1A_2$ is to one, the smaller the deviation of the experimental value from the actual value and only for $A_1(1/A_2 - 1) \to 0$ (or $F_1/F_2 \to 0$) and $T_2/T_1 \to 0$ (or $A_1\varepsilon_2/\varepsilon_1A_2 \to 1$) does the experimental value of the emissivity approximate its actual value.

When $A_1\varepsilon_2/\varepsilon_1A_2 < 1$, a more complex dependence on the specified quantities occurs. If the value of the ratio $\varepsilon_1^{ex}/\varepsilon_1 > 1$, the deviation of the experimental value ε_1^{ex} from the actual value ε_1 will be greater the greater the ratio T_2/T_1 and the smaller the values of the quantities $A_1\varepsilon_2/\varepsilon_1A_2$, $A_1(1/A_2 - 1)$, and of the ratio F_1/F_2. On the other hand, the deviation will be smaller the smaller the ratio T_2/T_1, the closer to one the value of the quantity $A_1\varepsilon_2/\varepsilon_1A_2$, and the greater the value of the quantity $A_1(1/A_2 - 1)$ and of the ratio F_1/F_2.

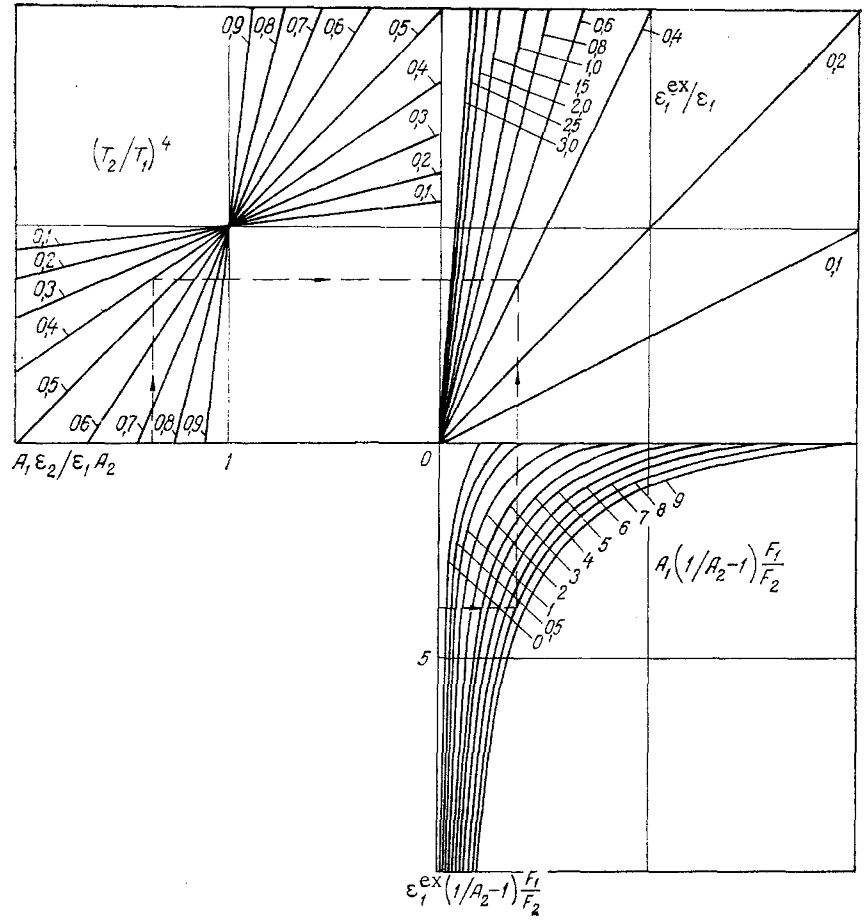

Fig. 2. Dependence of the ratio between experimental and actual values of emissivity on geometric, physical, and operational parameters [calculated from Eq. (5)].

If, however, $\varepsilon_1^{ex}/\varepsilon_1 < 1$, the deviation of ε_1^{ex} from ε_1 will be greater the smaller the ratio T_2/T_1, the closer to one the value of the quantity $A_1\varepsilon_2/\varepsilon_1 A_2$, and the greater the value of the quantity $A_1(1/A_2 - 1)$ and of the area ratio F_1/F_2. On the other hand, the deviation is smaller the closer the ratio T_2/T_1 is to one and the smaller the values of the quantities $A_1\varepsilon_2/\varepsilon_1 A_2$ and $A_1(1/A_2 - 1)$ and of the ratio F_1/F_2.

In all the cases discussed, the greater the value of the ratio F_1/F_2 and of the quantity $A_1(1/A_2 - 1)$ the greater the effect of a change in each of these quantities. The smaller the value of the quantity $A_1(1/A_2 - 1)$ the smaller the effect of the area ratio, and in the case $A_1(1/A_2 - 1) \to 0$, which can occur when $A_2 \to 1$, the ratio F_1/F_2 has no effect on $\varepsilon_1^{ex}/\varepsilon_1$ (the last case corresponds to the condition $F_1/F_2 \to 0$ discussed in [3]).

Since it is not known within what limits the ratios $A_1\varepsilon_2/\varepsilon_1 A_2$ and $\varepsilon_1^{ex}/\varepsilon_1$ fall, then by assuming that the values of $A_1\varepsilon_2/\varepsilon_1 A_2$ change considerably more slowly than those for T_2/T_1, an increase in accuracy when using Eq. (2) for the calculation of ε_1^{ex} should be achieved by performing an experiment under the conditions $T_2/T_1 \to 0$ and $F_1/F_2 \to 0$.

The experimental apparatus may be realized in such a way that it is impossible to neglect the ratio F_1/F_2 (two-cylinder method). As a rule, however, equality of emissivity and absorptivity of a body is assumed, i.e., $\varepsilon = A$. In such a case, the following equation is obtained from Eq. (1) as a starting point for the calculation of emissivity:

$$Q = \frac{\sigma_0 (T_1^4 - T_2^4) F_1}{1/\varepsilon_1 + (F_1/F_2)(1/A_2 - 1)} . \qquad (4)$$

Under the assumptions made, the deviation of the experimental value of emissivity from the actual value as determined from Eqs. (1) and (4) is given by

$$\frac{\varepsilon_1^{ex}}{\varepsilon_1} = \left[1 - \varepsilon_1^{ex}(1/A_2 - 1)\frac{F_1}{F_2}\right]\left[1 - \frac{A_1}{\varepsilon_1} \cdot \frac{\varepsilon_2}{A_2}\left(\frac{T_2}{T_1}\right)^4\right]\left[1 + A_1(1/A_2 - 1)\frac{F_1}{F_2}\right]\left[1 - \left(\frac{T_2}{T_1}\right)^4\right]^{-1} . \qquad (5)$$

The dependence of $\varepsilon_1^{ex}/\varepsilon_1$ on the parameters T_2/T_1, $A_1\varepsilon_2/\varepsilon_1A_2$, $A_1(1/A_2 - 1)(F_1/F_2)$, and $\varepsilon_1^{ex}(1/A_2 - 1)(F_1/F_2)$ is shown as a nomogram in Fig. 2. Each of these parameters is a quantity that is positive and greater than zero. It is clear from the nomogram (Fig. 2) that there is a complex dependence of $\varepsilon_1^{ex}/\varepsilon_1$ on the indicated parameters.

For $A_1\varepsilon_2/\varepsilon_1A_2 > 1$, just as for $A_1\varepsilon_2/\varepsilon_1A_2 < 1$, it is necessary to consider the cases $\varepsilon_1^{ex}/\varepsilon_1 < 1$ and $\varepsilon_1^{ex}/\varepsilon_1 > 1$. Thus, in the case $A_1\varepsilon_2/\varepsilon_1A_2 > 1$ when $\varepsilon_1^{ex}/\varepsilon_1 > 1$, the deviation of the experimental value from the actual value is smaller the closer to one the value of the ratio T_2/T_1, the greater than one the value of the quantity $A_1\varepsilon_2/\varepsilon_1A_2$, and the greater the quantity $A_1(1/A_2 - 1)(F_1/F_2)$ and the smaller the quantity $\varepsilon_1^{ex}(1/A_2 - 1)(F_1/F_2)$.

In the case $A_1\varepsilon_2/\varepsilon_1A_2 < 1$ when $\varepsilon_1^{ex}/\varepsilon_1 > 1$, the deviation of experimental value from the actual value decreases with a decrease in the quantities T_2/T_1 and $\varepsilon_1^{ex}(1/A_2 - 1)(F_1/F_2)$, an increase in the quantity $A_1(1/A_2 - 1)(F_1/F_2)$, and a trend toward one in the value of $A_1\varepsilon_2/\varepsilon_1A_2$; when $\varepsilon_1^{ex}/\varepsilon_1 < 1$, the deviation decreases with a trend toward zero for the value of $A_1\varepsilon_2/\varepsilon_1A_2$ and opposite changes in the other parameters.

Thus, an identical change of the same parameters does not have a unique effect on the accuracy of an experimental determination of emissivity, i.e., with realization of experimental apparatus by the two-cylinder method, one encounters considerable difficulties not only in the determination of possible deviation of the experimental value of emissivity from its actual value, but it is also extremely difficult to predict the most favorable conditions for performing an experiment in order to obtain the smallest deviation of the experimental value of emissivity from its actual value.

Only in the case $A_2 \to 1$ (black shell) do the quantities $\varepsilon_1^{ex}(1/A_2 - 1)(F_1/F_2)$ and $A_1(1/A_2 - 1)(F_1/F_2)$, and consequently the ratio F_1/F_2, have no effect and the ratio $\varepsilon_1^{ex}/\varepsilon_1$ is determined only by the values of the quantities $A_1\varepsilon_2/\varepsilon_1A_2$ and T_2/T_1. However, it is extremely difficult to predict a possible change in the quantity $A_1\varepsilon_2/\varepsilon_1A_2$. In such a case, the most advisable experimental conditions (for nongray bodies) must involve the realization of the smallest possible value for the ratio T_2/T_1.

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MODELING HETEROGENEOUS CHEMICAL REACTIONS UNDER THE ACTION OF A TURBULENT JET

G. S. Antonova

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The chemical reaction of a solution with a metallic surface is modeled by the physical process of mass transfer. The general form of solution of the equation of convective diffusion is found and the possibility of calculating parameter values for which the process will occur efficiently is examined. The results of analysis are confirmed by experimental data.

It has been known from the time of Nernst that, when a metal dissolves in an aqueous solution, in most cases the process occurs in the diffusional region, where the effect of the molecular constant of the solution is negligible [1]. However, it has not been possible to reach a final conclusion as to the region in which heterogeneous reaction occurs when a metallic surface dissolves under the action of perpendicular turbulent jets of aqueous solution, since until recently this situation had not been studied from the appropriate point of view.

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